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(54) A thickening agent and cosmetic compositions containing it

(57) A gelling or thickening agent is produced from the ionic interaction of:
a cationic polymer comprising a polymer of a cellulose, or a cellulose derivative, which is grafted with a quaternary ammonium salt of a water-soluble monomer, and
a carboxylic anionic polymer having a specified capillary viscosity and Epprecht-Drage viscosity.
The anionic polymer may be polymethacrylic acid, a copolymer of methacrylic acid with an alkyl acrylate or methacrylate, an acrylamide derivative, maleic acid, a monoalkyl maleate or N-vinyl pyrrolidone, or an ethylene-maleic anhydride copolymer.
The agent is incorporated in compositions for treating the hair, skin or nails e.g. hair rinsing or setting lotions, shampoos, anti dandruff compositions, anti seborrhoeic compositions, support gels for permanent waving, hair dyeing compositions, anti-acne compositions and antipsoriatic compositions.

GB 2 193 501 A

SPECIFICATION

A thickening agent and cosmetic compositions containing it

The present invention relates to a new gelling or thickening agent, new thickened or gelled cosmetic compositions containing such an agent and a process enabling cosmetic compositions to be gelled and/or thickened.

A general requirement existing in the cosmetics industry is for compositions for hair or for the skin which do not flow too quickly; such is the case, in particular, with the compositions employed in processes which involve periods of application or of contact of the composition with the hair or the skin. It is very advantageous, in this case, to employ compositions which have a viscosity index higher than a certain limit enabling the products to be properly localized with the aid of thickened solutions.

In previous patents such as French Patents 2,383,660, 2,505,179 and 2,542,997, we have already described compositions containing cationic polymers and anionic polymers in an aqueous medium capable of being presented in the form of thickened or gelled compositions. The polymers are employed in these compositions in order to impart to hair advantageous shape-retention, sheen and disentangling properties. These compositions are optionally thickened with a gelling or thickening agent which is added to the polymers.

Such gelled or thickened compositions of the prior art have the disadvantage, however, resulting from the presence of the gelling or thickening agents, of excessively loading the hair or of leaving an unattractive powdery deposit or, yet again, of imparting to it an unpleasant feel or a dull appearance, particularly when involving compositions whose application is not followed by a rinse.

These compositions, which contain a gelling or thickening agent in addition to the polymers, are sometimes cloudy or opaque, and this can prevent their use in certain applications such as, for example, hair-shaping compositions which are generally clear.

We have investigated the possibility of preparing gelled or thickened aqueous cosmetic compositions conferring onto hair the advantageous shape-retention and sheen properties of the compositions containing cationic and anionic polymers, while avoiding the abovementioned disadvantages due to the addition of gelling agents or thickeners.

It is known to form gels from a polymer derived from a quaternary ammonium of cellulose ether as described in US-A-3,472,840 and from an anionic polymer which is alginic acid or a polysulphonic acid such as 2-acrylamido-2-methylpropanesulphonic acid. The gelled compositions produced in this manner result, on the one hand, from the use of anionic polymers which themselves have thickening or gelling properties and, furthermore, require relatively high solids concentrations. Furthermore, such compositions are not completely satisfactory when they are employed for conditioning hair damaged by physical or chemical treatments or by atmospheric agents.

We have found that it is possible to prepare aqueous cosmetic compositions which are gelled or thickened by a copolymer of cellulose or of a cellulose derivative which are grafted by a radical route with a quaternary ammonium salt of a water-soluble monomer with certain carboxylic anionic polymers. This synergistic effect appears to be due, though this is merely a hypothesis, to the formation of an interpolymer by ionic interaction in an aqueous medium. To make the definition easier, the term "thickener" or "thickening agent" is employed in the remainder of the specification to denote a product having thickening and/or gelling properties resulting from this interaction.

The formation of a thickening agent is particularly surprising insofar as it results from polymers which do not individually have the thickening properties of the resulting agent. This capacity is markedly superior to that of gels known previously, some of which have been produced using anionic polymers which themselves have gelling properties. This is particularly advantageous within the scope of the present invention because the thickening characteristics make it possible not only to achieve a saving in the use of the polymers to obtain an identical gelling but at the same time make it possible to impart to the hair or to the skin, which are treated with these compositions, certain improved cosmetic properties without loading the hair excessively.

The cosmetic compositions containing the thickening agent have the advantage of not loading the hair, even when the applications are repeated, especially in the case of compositions which are applied using methods which do not involve a rinsing stage, and of imparting a pleasant feel and a gleaming appearance to the hair. They impart good shape retention and good liveliness to hair, and more particularly to fine hair, in the case of the compositions whose application is followed by a water rinse. Lastly, these compositions make it possible to improve the treatment of damaged hair, especially insofar as its disentangling, its softness and its feel are concerned.

The subject of the present invention concerns a thickener resulting from an ionic interaction in an aqueous medium of a copolymer of a cellulose or a cellulose derivative grafted by a radical route with a quaternary ammonium salt of a water-soluble monomer with a particular group of

carboxylic anionic polymers.

The present invention provides a gelling or thickening agent produced from the ionic interaction of:

a cationic polymer comprising a polymer of cellulose or a cellulose derivative which are grafted with a quaternary ammonium salt of a water-soluble monomer, and

a carboxylic anionic polymer having an absolute capillary viscosity, at a concentration of 5% in dimethylformamide or methanol at 30°C, of lower than or equal to 30×10^{-3} Pa s, this thickener having an Epprecht-Drage viscosity, module 3, of at least 0.45 Pa s in solution at a concentration of 1% in water at 21°C.

The ionic interaction is preferably carried out in an aqueous medium and the grafting is preferably carried out by a radical route. The cationic polymer preferably has an absolute capillary viscosity at 1% in water at 30°C of less than 0.025 Pa s.

The cationic polymer is preferably a cellulose, or hydroxyalkyl cellulose such as hydroxymethyl cellulose, hydroxyethyl cellulose or hydroxypropyl cellulose which are grafted by a radical route with a methacryloylethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt, more particularly a halide such as a chloride, or a methosulphate.

A particularly preferred cationic polymer is a hydroxyethyl cellulose copolymer grafted by a radical route with diallyldimethylammonium chloride sold under the trade name "Celquat L 200" or "Celquat H 100" by National Starch, which is also called "Polyquaternium 4" in the CFTA dictionary. When diluted to a concentration of 1% in water at a temperature of 30°C, this polymer has an absolute capillary viscosity of the order of 0.01 Pa s in the case of the product marketed under the trade name "Celquat L 200" or of 0.021 Pa s in the case of the product marketed under the trade name "Celquat H 100".

The carboxylic anionic polymer preferably has a molecular weight of from 500 to 3,000,000 more particularly from 1,000 to 3,000,000. It is preferably a film-forming polymer.

Particularly preferred polymers are:

(a) a methacrylic acid homopolymer which has a molecular weight of greater than 20,000, as determined by light scattering.

(b) a copolymer of methacrylic acid with one of the following monomers:

C_1–C_4 alkyl acrylate or methacrylate;

an acrylamide derivative, such as N,N-dimethylacrylamide, diacetoneacrylamide or N-tert-butylacrylamide;

maleic acid;

C_1–C_4 monoalkyl maleate; or

N-vinylpyrrolidone; or

(c) a copolymer of ethylene with maleic anhydride, such as the product sold under the trade name EMA 31 by Monsanto Cie.

Particularly preferred anionic polymers are methacrylic acid copolymers which have an absolute capillary viscosity measured at a concentration of 5% in solution in dimethylformamide or methanol, at 30°C, of from 0.003 to 0.030 Pa s, more particularly a copolymer of methacrylic acid with methyl methacrylate whose absolute capillary viscosity, measured at a concentration of 5% in solution in dimethylformamide, is of the order of 0.015 Pa s or a copolymer of methacrylic acid with monoethyl maleate which has an absolute capillary viscosity, measured at a concentration of 5% in solution in dimethylformamide, of the order of 0.013 Pa s, a copolymer of methacrylic acid with butyl methacrylate whose absolute capillary viscosity, measured at a concentration of 5% in solution in methanol, is of the order of 0.010 Pa s, or a copolymer of methacrylic acid with maleic acid whose absolute capillary viscosity, measured at a concentration of 5% in solution in dimethylformamide, is of the order of 0.016 Pa s.

The thickener may, for example, be prepared under the following conditions:

a quantity of water is added to the copolymer of cellulose or cellulose derivative grafted by a radical route with a quaternary ammonium salt of a water-soluble monomer to dissolve it (solution I).

Separately, a quantity of water is added to the carboxylic anionic polymer to dissolve it, the dissolution being promoted by neutralization with a conventional alkalifying agent such as aqueous ammonia or an alkanolamine (solution II).

The thickener may then be formed by adding solution I to solution II or vice versa, with stirring, at ambient temperature. When the gelling or thickening agent has formed it can then, if desired, be diluted with water or with a mixture of water and alcohol, the proportion of alcohol being that required to produce the required alcoholic strength for the formulation.

According to an alternative form of this process, it is equally possible, without recourse to neutralization, to dissolve the carboxylic anionic polymer in alcohol, preferably ethanol, at a concentration such as to bring the final formulation to the alcoholic strength required.

The thickener may also be formed in the aqueous cosmetic medium itself.

The copolymer of cellulose or a cellulose derivative which are grafted with a quaternary ammonium salt is preferably used in an aqueous medium, generally in an amount of from 0.01

to 6%, especially 0.1 to 1.5%, by weight relative to the weight of the composition. The carboxylic anionic polymer is preferably used in an aqueous medium, generally in an amount of from 0.01 to 6%, especially 0.1 to 1.5%, by weight relative to the weight of the composition. The weight ratio of the cationic polymer to the carboxylic anionic polymer is preferably from 1:5 to 5:1, more preferably from 1:2 to 2:1 and is especially equal to about 1:1.

The present invention also provides a cosmetic composition suitable for the treatment of hair, skin or nails which comprises at least one gelling or thickening agent as defined above and at least one further adjuvant.

The thickener is preferably present in the composition of the present invention in a concentration of from 0.02 to 12%, more preferably from 0.2 to 3%, by weight based on the total weight of the composition.

This composition is generally in aqueous form, but may contain other cosmetically acceptable solvents such as, for example, lower (for example C_1–C_8 or C_1–C_4) alcohols such as ethanol or isopropanol, glycerol, glycols or glycol ethers such as ethylene glycol monobutyl ether, propylene glycol, diethylene glycol monoethyl ether and monomethyl ether, in proportions which do not affect the formation of the thickener.

These compositions have a pH which is generally from 6 to 12, preferably from 6.5 to 9, more particularly, close to neutrality, for example of the order of 7 to 8.

The pH may be adjusted with an alkalifying or acidifying agent which is usually employed in the field of cosmetics.

The cosmetic composition may, for example, be employed as a shampoo, after-shampoo composition, product for rinsing to be applied before or after shampooing, before or after dyeing or bleaching, before or after permanent-waving or hair straightening, a hair-setting or blow-drying composition, a restructuring composition, or a support for permanent-waving or for dyeing or bleaching hair. The composition may also contain a dermatological active principle such as an antidandruff, antiseborrhoeic, antiacne, antifungal, bactericidal, keratolytic or antipsoriatic agent.

When the composition is in the form of a thickened lotion or gel for hair-setting or for blow-drying, it may optionally contain other polymers which are usually employed in a composition of this type, more particularly nonionic polymers such as polyvinylpyrrolidones, copolymers of polyvinylpyrrolidone with vinyl acetate, or anionic polymers which do not have the abovementioned properties of gelling or thickening with the cationic polymer, for example copolymers of vinyl acetate with an unsaturated carboxylic acid such as crotonic acid, copolymers resulting from the copolymerization of vinyl acetate with crotonic acid and an acrylic or methacrylic ester, copolymers resulting from the copolymerization of vinyl acetate with an alkyl vinyl ether and an unsaturated carboxylic acid and copolymers resulting from the copolymerization of vinyl acetate with crotonic acid and a vinyl ester of an acid containing a long carbon chain or an allyl or methallyl ester of an acid containing a long carbon chain. These polymers are generally employed in a concentration of from 0.1 to 5% by weight based on the total weight of the composition.

When employed as a rinsing composition, the composition may contain various conditioning agents such as quaternary proteins, cationic silicone polymers, cationic surfactants and cationic polymers other than polymers of cellulose or of cellulose derivatives grafted by a radical route with a quaternary ammonium water-soluble monomer, of the polyamine, polyaminoamide or quaternary polyammonium type.

When the compositions are employed as shampoos, they may contain surface-active agents with detergent properties which are known per se, such as anionic, cationic, nonionic or amphoteric surface-active agents or mixtures thereof.

In general, the surface-active agents are present in a proportion of from 0.1 to 30% by weight based on the total weight of the composition.

When the composition is employed for dyeing hair, it may contain a direct dye or oxidation dye precursor which is known in the art.

The compositions may also be used for conditioning skin and nails.

A particularly perferred cosmetic composition is a hair-shaping composition which is not rinsed off. This composition comprises, in an aqueous or aqueous-alcoholic medium, a thickener resulting from the ionic interaction of 0.1 to 1.5% by weight of a hydroxyethyl cellulose copolymer grafted by a radical route with diallyldimethylammonium chloride and 0.1 to 1.5% by weight of a copolymer of methacrylic acid with methylmethacrylate or with monoethyl maleate or with butyl methacrylate whose absolute capillary viscosity, measured at 30°C in solution in dimethylformamide or methanol at a concentration of 5%, is from 0.010 to 0.015 Pa s, the Epprecht-Drage viscosity of the thickener, measured at 21°C, module 3, diluted to a concentration of 1% in water, being higher than 0.45 Pa s, and the pH of the composition being from 6.5 to 9.

The compositions according to the invention may contain any other ingredient which is usually employed in cosmetics, such as perfumes, colourants, preservatives, sequestering agents, softeners or silicones.

The present invention also provides a process for thickening or gelling a cosmetic composition

wherein at least one thickener as defined above or a composition containing the polymers forming the thickener in a proportion of from 0.02 to 12% by weight based on the total weight of the composition is introduced into the composition to give it an Epprecht-Drage viscosity, measured at 21°C (module 3), of at least 0.450 Pa s.

Aqueous gels or thickened compositions containing the thickener may be prepared separately, and the cosmetic composition may be prepared in a different step, if desired at the time of use.

The present invention also provides a process for the treatment of hair, of the skin and of the nails, wherein a cosmetic composition as defined above is applied thereto, it being possible for this composition to be rinsed off with water, or not, according to the nature of the treatment desired.

We have found that the composition for the treatment of hair not only makes it possible to localize the product on hair properly without flowing onto the face but that the hair treated in this manner also has a pleasant feel and a shiny appearance. Furthermore, the thickened or gelled composition has the advantage of being clear.

The examples which follow further illustrate the invention.

EXAMPLE 1

Aqueous gels were prepared according to the information which appears in Table A which follows. For this purpose 50 cm^3 of an aqueous solution containing 1% of active substance of the product marketed under the trade name of "Celquat L 200", which is a copolymer of hydroxyethyl cellulose grafted by a radical route with diallyldimethylammonium chloride, were added at ambient temperature and with mechanical stirring to 50 cm^3 of an ethanolic solution at an alcohol strength of 20° containing 1% as active substance of the previously neutralized anionic polymer defined in the table.

In Table A below, the measurement of the absolute capillary viscosity of the anionic polymers is carried out in dimethylformamide (DMF) and/or in methanol.

TABLE A

INITIAL MIXTURE				Epprecht-Drage viscosity of the thickener formed Pa s
CATIONIC POLYMER		Absolute capillary viscosity Pa s x 10^{-3}		(3)
CELQUAT L 200		(1) 10.4		
CARBOXYLIC ANIONIC POLYMER	Proportions	(2) DMF	CH_3OH	
Methacrylic acid/methyl methacrylate copolymer	50/50	15		1.550
" " "	80/20	24.47	10.56	1.430
Methacrylic acid/methyl acrylate copolymer	50/50		16.4	1.300
" " "	80/20	17.7	8.5	1.150
Methacrylic acid/butyl methacrylate copolymer	85/15		9.94	2.000
Methacrylic acid/monoethyl maleate copolymer	63.6/36.4	3.46		0.620 (mod 4)
" " "	59/41	8		1.000 (mod 4)
" " "	66/34	19.2		0.780;1.500 (mod 4)
" " "	61/39	26.8		0.580;1.250 (mod 4)
" " "	62/38	10.4		0.550;1.000 (mod 4)
" " "	65/35	14.1		0.800;1.200 (mod 4)
" " "	63/37	13		1.490;2.000 (mod 4)
" " "	66/34	12		1.700;2.100 (mod 4)
" " "	68/32	19.2		1.700;2.500 (mod 4)
" " "	72/28	14.2		1.280;1.500 (mod 4)
Methacrylic acid/N,N-dimethylacrylamide copolymer	50/50			0.980
" " "	80/20	16.3		1.350
Methacrylic acid/diacetoneacrylamide copolymer (4)	80/20		1.07	1.200
Methacrylic acid/N-tert-butylacrylamide copolymer	80/20		4.06	1.050
Methacrylic acid/maleic acid copolymer	65/35	16.7		2.100
" " "	70/30	13.6		1.800
Methacrylic acid/N-vinylpyrrolidone copolymer	80/20	9.2		1.050
Polymethacrylic acid MW 137,000			6.8	1.400
" " MW 186,000			9.8	2.100
Ethylene/maleic anhydride copolymer Monsanto EMA 31		9.82	8.15	1.600

(1) measured at 30°C in 1% strength solution in water

(2) measured at 30°C in 5% strength solution in dimethylformamide or methanol

(3) module 3 - measured at 21°C in 1% strength 10° aqueous alcohol solution - pH = 7.5

(4) viscosity measured using a 1% strength solution of this anionic polymer.

EXAMPLES 2 to 11

The following gelled compositions for hair styling are prepared (Tables B and C).

When these various compositions are applied to clean wet hair, they impart shape retention to it without leaving a powdery deposit. When they are applied to dried hair it is found that the composition makes styling easier without loading the hair and that, once dried, the latter is soft and has a pleasant feel.

TABLE B

COMPOSITIONS	EXAMPLE No.				
	2	3	4	5	6
Celquat H 100 g % AS	0.5	0.4			
Celquat L 200 g % AS			0.8	1	0.3
Methacrylic acid/monoethyl maleate copolymer (66/34) g % AS	0.5				
Methacrylic acid/maleic acid copolymer (70/30) g % AS		0.6			
Methacrylic acid/butyl methacrylate copolymer (85/15) g % AS			0.8		
Polymethacrylic acid MW 137,000 g % AS					0.4
Ethylene/maleic anhydride copolymer Monsanto EMA 31 g % AS				0.8	
2-Amino-2-methyl-1-propanol q.s. pH	8	9	7	6	9
Ethyl alcohol q.s.	20°		25°		10°
Water q.s. g	100	100	100	100	100
Epprecht-Drage viscosity 21°C 1% in H_2O (module 3) in Pa s	1.150	0.700	2.150	2.400	0.725

TABLE C

COMPOSITIONS	EXAMPLE No. 7	8	9	10	11
Celquat H 100 g % AS	0.4			0.5	
Celquat L 200 g % AS		1	0.66		0.33
Methacrylic acid/N-tert-butylacrylamide copolymer 80/20 g % AS	0.2				
Methacrylic acid/N,N-dimethyl acrylamide copolymer 80/20 g % AS		0.5			
Methacrylic acid/methyl methacrylate copolymer 50/50 g % AS			0.33		
Methacrylic acid/methyl methacrylate copolymer 80/20 g % AS				1	
Polymethacrylic acid MW 186,000 g % AS					0.66
2-Amino-2-methyl-1-propanol q.s. pH	8	8.5	7.5	8.5	7.5
Ethyl alcohol q.s.		30°	10°	10°	10°
Perfume, colorant, preservative					
Water q.s. g	100	100	100	100	100
Epprecht-Drage viscosity 21°C 1% in H_2O (module 3) in Pa s	0.480	1.800	0.900	1.725	1.300

EXAMPLE 12

An after-shampoo of the following composition is prepared:

(A) Celquat L 200 from National Starch		0.7	g As
(B) 72/28 Methacrylic acid/monoethyl maleate copolymer		0.7	g As
Distearyldimethylammonium chloride		1	g
Hydrochloric acid	q.s. pH: 7		
Water	q.s.	100	g

This composition is applied to clean, roughly dried hair. After being left in place for a few minutes it is rinsed off with water. The wet hair is smooth and slippery. After drying it is lively and has body.

The gel obtained by interaction of the two polymers A and B has an Epprecht-Drage viscosity at 21°C, module 3, of 1.7 Pa s at a concentration of 1.4% in water.

EXAMPLE 13

An after-shampoo of the following composition is prepared:

(A) Celquat L 200 from National Starch		0.7	g AS
(B) 50/50 Methacrylic acid/methyl methacrylate copolymer		0.7	g AS
Quaternized protein sold under the trade name of "Lexein QX 3000" by Inolex		1	g AS.
Hydrochloric acid	q.s. pH: 6.7		
Water	q.s.	100	g

This gelled composition is applied to clean, roughly dried hair. After being left in place for a few minutes it is rinsed off with water.

The dried hair is lively and has body.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 3, of 1.8 Pa s at a concentration of 1.4% in water.

EXAMPLE 14

The following shampoo is prepared:

(A) Celquat L 200 from National Starch		0.5	g AS
(B) 50/50 Methacrylic acid/methyl methacrylate copolymer		0.7	g AS
Nonionic surfactant of formula:			
$R–CHOH–CH_2O–[CH_2–CHOH–CH_2O]_n–H$			
in which			
R denotes a mixture of C_9–C_{12} alkyl radicals			
n denotes a statistical mean value of about 3.5		10	g AS
Hydrochloric acid	q.s. pH: 7.4		
Perfume, preservative	q.s.		
Water		100	g

This shampoo has the appearance of a clear gel.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 3, of 1.65 Pa s at a concentration of 1% in water.

EXAMPLE 15

The following shampoo is prepared:

(A) Celquat L 200 from National Starch		0.7	g AS
(B) 72/28 Methacrylic acid/monoethyl maleate copolymer		0.7	g AS
Sodium alkyl ether carboxylate oxyethylenated with 3 moles of ethylene oxide, sold by Marchon under the trade name "Empilan 2747/30"		10	g AS
Hydrochloric acid	q.s. pH: 6		
Perfume, preservative	q.s.		
Water	q.s.	100	g

This shampoo has the appearance of a clear gel.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°, module 3, of 1.7 Pa s at a concentration of 1.4% in water.

EXAMPLE 16

The following lotion is prepared:

(A) Celquat L 200		0.1	g
(B) Polymethacrylic acid		0.1	g
2-Amino-2-methyl-1-propanol	q.s. pH: 7.5		
Perfume, colorant, preservative	q.s.		
Water	q.s.	100	g

This hair-setting lotion is slightly gelled and does not require rinsing.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 2, of 0.095 Pa s at a concentration of 0.2% in water.

EXAMPLE 17

The following antidandruff composition is prepared:

(A) Celquat L 200		1.5	g
(B) 66/34 Methacrylic acid/monoethyl maleate copolymer		1.2	g
1-Hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2-(1H)-pyridinone, ethanolamine salt, sold under the trade name "Octopirox" by Hoechst		0.1	g
Ethyl alcohol	q.s. 30°		
2-Amino-2-methyl-1-propanol	q.s. pH 7		
Preservative, perfume	q.s.		
Water	q.s.	100	g

This antidandruff composition has the appearance of a clear gel and it does not require rinsing.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 3, of about 1.8 Pa s at a concentration of 2.7% in water.

EXAMPLE 18

The following antiseborrhoeic composition is prepared:

(A) Celquat L 200		0.5	g
(B) 50/50 Methacrylic acid/methyl methacrylate copolymer		0.5	g
Poly-β-alanine		1	g
2-Amino-2-methyl-1-propanol	q.s. pH 10		
Preservative, perfume	q.s		
Water	q.s.	100	g

This antiseborrhoeic composition which can be applied to the skin or to hair has the appearance of a clear gel and does not require rinsing.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 3, of about 1.2 Pa s at a concentration of 1% in water.

EXAMPLE 19

The support gel for permanent-waving, of the following composition, is prepared:

Composition 1

Glycerol monothioglycolate		68.3	g
Glycerin	q.s.	100	g

Composition 2

Celquat L 200		1.8	g
70/30 Methacrylic acid/maleic acid copolymer		1.5	g
2-Amino-2-methyl-1-propanol	q.s. pH 6.5		
Triethanolamine		3	g
Perfume, colorant, preservative	q.s.		
Water	q.s.	100	g

The two compositions 1 and 2 are mixed ad hoc in proportions of 32 g of composition 1 to 87 g of composition 2.

This mixture is applied to hair which is wound onto rollers, for 15 minutes. After 15 minutes in place, it is rinsed off and an oxidizing solution consisting of 8-volume hydrogen peroxide, pH 3, is applied for 10 minutes.

The hair is then rinsed.

EXAMPLE 20

The following direct-dyeing composition is prepared:

50/50 Methacrylic acid/methyl methacrylate copolymer		0.5	g AS
Celquat L 200 from National Starch		0.5	g AS
1-N-(γ-hydroxypropyl)amino-2-nitro-4-N',N'-bis(β-hydroxyethyl)aminobenzene monohydrochloride		0.1	g
2-Amino-2-methyl-1-propanol	q.s. pH 7.5		
Ethyl alcohol	q.s. 10°		
Preservative	q.s.		
Water	q.s.	100	g

This dyeing composition is applied to wet brown hair, washed beforehand. After drying, the hair acquires an ashen brown color.

EXAMPLE 21

The antipsoriatic composition is prepared by adding 0.5 g of anthraline at the time of use to the gel of the following composition:

(A) Celquat L 200		0.5	g
(B) 50/50 Methacrylic acid/methyl methacrylate copolymer		0.5	g
2-amino-2-methyl-1-propanol	q.s. pH 7		
Ethyl alcohol	q.s. 10°		
Preservative	q.s.		
Water	q.s.	100	g

The antipsoriatic composition is applied to the skin and does not require rinsing.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 3, of about 1.2 Pa s at a concentration of 1% in water.

EXAMPLE 22

The following antiacne composition is prepared by adding 5 g of benzoyl peroxide at the time of use to the gel whose composition is given in Example 21.

The composition is applied to the skin.

EXAMPLE 23

The following bactericidal composition is prepared by adding 1 g of 5-chloro-2-(2,4-dichlorophenoxy)phenol or triclosan (DCI) sold under the name of "Irgasan DP 300" at the time of use to the gel whose composition is given in Example 21.

This composition is applied to the skin.

EXAMPLE 24

A hair-conditioning composition is prepared by adding 18 g of iris powder diluted with 36 g of water to 46 g of a gel of the following composition:

(A) Celquat L 200		4.5	g
(B) 80/20 Methacrylic acid/N-vinylpyrrolidone copolymer		4.5	g
Ethyl alcohol	q.s. 10°		
2-Amino-2-methyl-1-propanol	q.s. pH 7.5		
Perfume, preservative	q.s.		
Water	q.s.	100	g

The composition is applied to washed hair. After rinsing, the hair has a soft feel.

The gel obtained by interaction of the polymers A and B has an Epprecht-Drage viscosity at 21°C, module 4, of 11.7 Pa s at a concentration of 9% in water.

EXAMPLE 25

The following restructuring rinsing lotion is prepared by adding 1.5 g of dimethylolethylenethiourea at the time of use to the gel of Example 21 at pH 6.

This composition is applied to damaged hair.

CLAIMS

1. A gelling or thickening agent produced from the ionic interaction of:

a cationic polymer comprising a polymer of a cellulose or a cellulose derivative which are grafted with a quaternary ammonium salt of a water-soluble monomer, and

a carboxylic anionic polymer having an absolute capillary viscosity, at a concentration of 5% in dimethylformamide or methanol at 30°C, of lower than or equal to 30×10^{-3} Pa s, this thickener having an Epprecht-Drage viscosity, module 3, of at least 0.45 Pa s in solution at a concentration of 1% in water at 21°C.

2. An agent according to claim 1 wherein the cationic polymer is a hydroxyalkyl cellulose copolymer grafted by a radical route with a quaternary ammonium salt of a water-soluble monomer which is a methacryloylethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt.

3. An agent according to claim 1 or 2, wherein the carboxylic anionic polymer is:

a methacrylic acid homopolymer having a molecular weight greater than 20,000, as determined by light scattering,

a copolymer of methacrylic acid with a C_1–C_4 alkyl acrylate or methacrylate, an acrylamide derivative, maleic acid, a C_1–C_4 monoalkyl maleate or N-vinylpyrrolidone, or

a copolymer of ethylene with maleic anhydride.

4. An agent according to any one of claims 1 to 3 wherein the anionic polymer is:
a copolymer of methacrylic acid with methyl methacrylate whose absolute capillary viscosity, measured in solution in dimethylformamide at a concentration of 5% at 30°C, is of the order of 15×10^{-3} Pa s,
a copolymer of methacrylic acid with monoethyl maleate having an absolute capillary viscosity, measured in solution in dimethylformamide at a concentration of 5% at 30°C, of the order of 13×10^{-3} Pa s,
a copolymer of methacrylic acid with butyl methacrylate whose absolute capillary viscosity, measured in solution in methanol at a concentration of 5% at 30°C, is of the order of 10×10^{-3} Pa s, or
a copolymer of methacrylic acid with maleic acid whose absolute capillary viscosity, measured in solution in dimethylformamide at a concentration of 5% at 30°C, is of the order of 16×10^{-1} Pa s.

5. An agent according to any one of claims 1 to 4 wherein the weight ratio of the cationic polymer to the carboxylic anionic polymer is from 1:5 to 5:1.

6. An agent according to any one of claims 1 to 5 which has been prepared in an aqueous medium comprising 0.01 to 6% of the cationic polymer and 0.01 to 6% of the carboxylic anionic polymer.

7. An agent according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

8. A cosmetic composition suitable for the treatment of hair, skin or nails, which comprises at least one gelling or thickening agent as defined in any one of claims 1 to 7 and at least one further adjuvant.

9. A composition according to claim 8 wherein the gelling or thickening agent is present in a proportion of from 0.02 to 12% by weight based on the total weight of the composition.

10. A composition according to claim 8 or 9, which has a pH of from 6 to 12.

11. A composition according to any one of claims 8 to 10 suitable for use as a thickened or gelled lotion for hair-setting or for blow-drying which additionally comprises a nonionic polymer which is a polyvinylpyrrolidone or copolymer or polyvinylpyrrolidone with vinyl acetate, or an anionic polymer which is a copolymer of vinyl acetate with an unsaturated carboxylic acid, a copolymer resulting from the polymerization of vinyl acetate with crotonic acid and an acrylic or methacrylic ester, a copolymer resulting from the copolymerization of vinyl acetate with a vinyl alkyl ether and an unsaturated carboxylic acid, a copolymer resulting from the copolymerization of vinyl acetate with crotonic acid and a vinyl ester of an acid containing a long carbon chain or an allyl or methallyl ester of an acid containing a long carbon chain.

12. A composition according to any one of claims 8 to 11 in the form of a shampoo which comprises one or more anionic, cationic, nonionic or amphoteric surface-active agents with a detergent property.

13. A composition according to any one of claims 8 to 10, suitable for rinsing off, which comprises a conditioning agent which is a quaternary protein, cationic silicone polymer, cationic surfactant or cationic polymer other than a polymer of a cellulose or cellulose derivative grafted by a radical route with a quaternary ammonium water-soluble monomer.

14. A cosmetic composition suitable for use in hair-setting, which comprises, in an aqueous or aqueous-alcoholic medium, a thickener resulting from the ionic interaction of 0.1 to 1.5% by weight of a hydroxyethyl cellulose copolymer grafted by a radical route with diallyldimethylammonium chloride and 0.1 to 1.5% by weight of a copolymer of methacrylic acid with methyl methacrylate or with monoethyl maleate or with butyl methacrylate whose absolute capillary viscosity, measured at 30°C in solution in dimethylformamide or methanol at a concentration of 5%, is from 0.010 to 0.015 Pa s, the Epprecht-Drage viscosity of the thickener, measured at 21°C, module 3, diluted to a concentration of 1% in water, being higher than 0.45 Pa s, and the pH of the composition being from 6.5 to 9.

15. A cosmetic composition according to claim 8 or 14 substantially as hereinbefore described with reference to any one of the Examples.

16. A process for thickening or gelling an aqueous cosmetic composition wherein at least one thickener as defined in any one of claims 1 to 7 is introduced into the composition to give it an Epprecht-Drage viscosity measured at 21°C (module 3) of at least 0.45 Pa s at a concentration of 1% in water.

17. A process for the treatment of hair, of the skin or of the nails, wherein at least one cosmetic composition as defined in any one of claims 8 to 15 or produced by a process as defined in claim 16 is applied thereto.

18. A process according to claim 17 wherein a composition as defined in claim 11 or 14 is applied, this application not being followed by a rinse.

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